Aerosol Chemical Composition Determined on Board the DOE G-1 Aircraft during MAX-Mex in March 2006

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OVERVIEW:

Aerosol chemical composition was determined on board the DOE G-1 aircraft along with particle size-number distributions and photochemically important trace gas species during the 2006 MAX-Mex/MILAGRO field campaign conducted over the Mexico City basin. The primary objective of this research is to identify and quantify the aerosol chemical components and their sources and to gain scientific understanding of the processes governing their formation and distributions. A detailed description of the G1 measurements and the flight tracks can be found in Stephen Springston's poster presentation.

TECHNIQUES:

Two different measurement techniques were deployed, namely, a Time-of-Flight Aerosol Mass Spectrometer (ToF-AMS) and a Particle-into-Liquid Sampler-Ion Chromatography (PILS-IC) technique. Their measurement characteristics are given below.

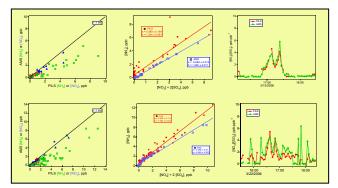
	Ionic Species Determined	Organic Species Determined	Time Resolution	Limit of Detection		
ToF-AMS	SO ₄ ²⁻ , NO ₃ -, NH ₄ +, Cl ⁻	Total Organics	12 s	~0.05 µg/m³		
PILS-IC	SO ₄ ²⁻ , NO ₃ -, NH ₄ +, Cl ⁻ Na ⁺ , Mg ²⁺ , Ca ²⁺ , K ⁺	-	180 s	~0.15 µg/m³		

RESULTS:

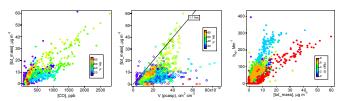
<u>Data Coverage.</u> Valid data were obtained on flights (identified with the day in March) with a check mark in the table below (☑ indicates possible underestimates due to leaks). Data analysis presented in this poster is based on the AMS measurement (for 8 selected flights) because of its fast time resolution, the ability to determine the organics, and a more complete time coverage. Note that AMS data are reported with a collection efficiency (CE) of 1.

G1 Flight	03A	06A	07A	09A	09B	15A	15B	18A	19A	19B	20A	20B	22A	25A	27A
Tof-AMS		✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓		
PILS-IC						✓	✓	☑	☑	☑	☑	☑	✓	✓	✓
This work		•1	•2			•3		•4	•5		•6	•7	•8		

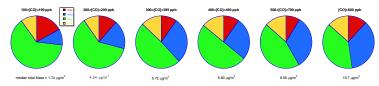
 $\underline{\text{Comparison between AMS and PILS.}} \quad \text{Examples are shown below for two flights, } 060315A \text{ and } 060322A.}$



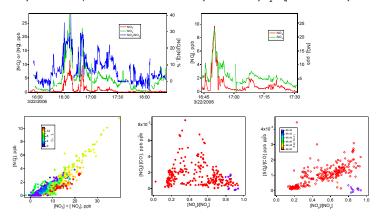
<u>Total Aerosol Mass Concentration.</u> The total aerosol mass concentration observed in the Mexico City Basin (Long < -98.28 deg) showed a fairly strong correlation with CO and the light scattering coefficients. The larger scatter observed in the middle graph (total mass vs PCASP particle volume) may be due to different size cuts of the AMS and the PCASP.



Composition. Aerosol NO₃ fraction decreases markedly with aging and dilution using CO as a reference. In contrast, the organic fraction increased from ~1/3 to ~2/3 with aging.

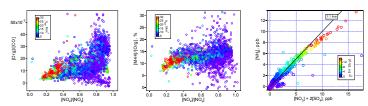


 $\underline{\text{NO}_3}$ and $\underline{\text{SO}_4}$ Production. Aerosol $\underline{\text{NO}_3}$ formation in urban plumes is very rapid as the fast AMS measurement revealed that the $\underline{\text{NO}_3}$ time profile matched that of $\underline{\text{NO}_2}$ perfectly. Although a significant portion of the $\underline{\text{NO}_2}$ is converted to aerosol $\underline{\text{NO}_3}$ in the plume (with a temperature dependency), $\underline{\text{NH}_4}\underline{\text{NO}_3}$ is lost by volatilization upon dilution with cleaner air and by acidification by $\underline{\text{H}_2}\underline{\text{SO}_4}$ that is continually



formed from ${\rm SO_2}$ oxidation. This chemical displacement is clearly illustrated by the data collected on 3/20/06: ${\rm SO_4}$ increased with age accompanying the ${\rm NO_3}$ loss.

<u>Organic Aerosol.</u> Organics comprised a significant portion of the aerosol mass (see the pie charts) and is seen to increase with photochemical age. The formation of this SOA may have not been strongly catalyzed by acid as the NO_3 and SO_4 were essentially neutralized by NH_4 . The fact that the ratio of the oxidized fraction (represented by the m/z 44 fragment) to the total organics remained fairly constant suggests that SOA results from condensation onto particles of gaseous organic compounds, rather than from oxidation of primary organic aerosols.



<u>Aerosol Sources</u> Aerosol NH $_4$, NO $_3$, and organics are seen to have strong sources in urban/industrial emissions; SO $_4$ is produced from SO $_2$ mainly emitted from point sources but spread over the geographical region due to its long lifetime. Although biomass burning and dusts are believed to be important aerosol sources, neither K nor Ca were detected, indicating that they might not be the best tracers for these sources in this region.

TENTATIVE CONCLUSIONS:

- 1. An Aerodyne ToF-AMS was successfully deployed on the G1 aircraft, measuring aerosol SO_4 , NO_3 , NH_4 , CI, and organics at a fast time resolution of 12 s.
- Regarding quantification, the AMS data are consistent with a collection efficiency of 0.5, a value similar to that observed in previous field studies.
- 3. $\rm NH_4NO_3$ is formed rapidly in urban plumes and exhibited a time profile in perfect sync with $\rm NO_2$, implying sufficient $\rm NH_3$ is available.
- 4. Although SO₄ concentration increased with photochemical age, it doesn't show appreciable correlation with large SO₂ plumes consistent with a slower oxidation rate compared to NO_x, allowing it to be spread to a larger geographical area.
- $5. \, NO_3$ concentration often showed a maximum on the photochemical age scale between 0.3 and 0.7 defined as NO_2/NO_y . The disappearance of aerosol NO_3 in aged air is consistent with its volatility in air of low concentrations of NO_3 and NO_3 , and with acidification by addition of NO_3 .
- Organics comprised an important fraction of aerosol mass, which increased with photochemical age with concomitant enhancement of the oxidized fraction indicated by the m/z 44 fragment. The primary organic component, indicated by m/z 57, typically showed a decline with age.
- 7. The aerosols were not strongly acidic as ${\rm NO_3}$ and ${\rm SO_4}$ were neutralized by ${\rm NH_4}$, consistent, in fact, with the presence of ${\rm NH_4NO_3}$.
- 8. Biomass burning and dust emissions are believed to be important aerosol sources in the Mexico City basin. However, since K and Ca were always below their limits of detection, they may not be the suitable tracers for these sources in this region.

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